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April 5, 2002

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DELIVERED BY HAND

Dear Sir:

Please file the attached specification as a new **provisional** patent application:

Title:	**VAPOR-ASSISTED CRYOGENIC CLEANING**
Attorney's docket no.:	**PAT 51857P-2**
Fees:	**Please charge to the Borden Ladner Gervais LLP deposit account no. 501593 in the amount of $160** to cover the large entity filing fee. Any deficiency or overpayment should also be charged or credited to this deposit account. **An extra copy of this page is attached.**
Entitled to small entity fees?	No
No. of pages in specification:	Three (3)
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We look forward to confirmation of filing in due course.

Yours very truly,

Borden Ladner Gervais LLP

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IP-KIT-1/3173.1

VAPOR-ASSISTED CRYOGENIC CLEANING

BACKGROUND OF THE INVENTION

Field of the Invention

The invention proposes to use a vapor with or without free radical generator, either simultaneously or sequentially with CO_2 snow cleaning to aid in removal of foreign materials (FM), e.g. particles and other contaminants, from semiconductor surfaces and other surfaces involved in precision cleaning.

The demands for greater switching speed and circuit performance have seen the advent of new dielectric materials (dielectric constant of <3) and metals to reduce the RC delay constant in circuits. The metal of choice, copper, has added several challenges to the process integration scheme. Unlike with aluminum interconnects where the metal patterning was performed with reactive ion etching (RIE) followed by dielectric deposition,. with copper, the dielectric is first deposited and etched to form vias and trenches followed by deposition of copper in those features. The excess copper is then removed using chemical mechanical polishing (CMP) to planarize the surface for subsequent layers of film. The copper inside the features needs to be prevented from migrating into the adjacent dielectric film as copper has high electrical mobility and can therefore cause metal shorts when a voltage is applied. In order to prevent the copper from diffusing into the dielectric film, a barrier layer of TaN is deposited on the sidewall of the features prior to filling them with copper. This method of forming copper interconnects for the back-end-of-line (BEOL) is known as the Dual Damascene process. Following the dielectric etch to form the vias and trenches, a large amount of fluoropolymeric residue is left both on the surface of the wafer and inside the features as seen in Figure 1. This residue needs to be cleaned before the TaN film and the copper deposition can be performed.

The dimensions of the features used in the interconnects at the BEOL are currently around 0.18 um. For the CO_2 snow cleaning to work effectively in removing the sidewall residues inside the features, Figure 1, it will imply that snow particles of less than 0.18 um will have to arrive at the surface of the wafer with enough velocity to impart the momentum transfer required to dislodge the sidewall residue. The flow of the CO_2 gas creates a boundary layer on the wafer surface. Assuming the thickness of the boundary layer to be h, a snow particle must enter the layer with a normal component of velocity equal to at least h/t where t is the time taken to cross the boundary layer and arrive at the wafer surface. The relaxation time of the particle crossing the boundary layer is given as (1)

$$\tau = \frac{2a^2\rho_p C_c}{9\eta} \qquad (1)$$

where:

a is the particle radius

ρ_p is the particle density

η is the viscosity of the gas

C_c is the Cunningham slip correction factor given as in (2)

$$C_c = 1 + 1.246(\lambda/a) + 0.42(\lambda/a)\exp[-0.87(a/\lambda)] \qquad (2)$$

where λ is the mean free path of gas molecules. Since the cryogenic CO_2 cleaning is at atmospheric pressure, the Cunningham slip correction factor becomes equal to 1 in equation 1.

Thus for snow particles to have sufficient momentum to perform removal of FM from the wafer surface and inside the features, the time to cross the boundary layer must be less than the relaxation time in which case they will arrive at the surface with at least 36% of the initial velocity. Equation 1 shows that the relaxation time decreases as the particle size becomes small. This implies that the small particles will not be able to arrive at the wafer surface with sufficient velocity for effective cleaning of the submicron vias and trenches.

Prior Art

The prior art involves the use of CO_2 or Argon cryogenic spray for removing FM from surfaces (Aerosol Surface Processing, Rose et. al., Pat#5,931,721; Substrate Cleaning Method and Apparatus, Aoki, Pat. #6,036,581; Photoresist and redeposition removal using carbon dioxide jet spray, Bowers, Pat. #5,853,962; Aerosol Surface Processing, Rose et. al., Pat. #6,203,406; High Dispersion Carbon Dioxide Snow Apparatus, Zito, Pat. # 5,775,127). In all of the above prior art, the FM are removed by physical force involving momentum transfer to the contaminants. Since there is no chemical component to the cleaning mechanism, this process is ineffective for removing small submicron particles and complex polymeric residues as generated by dielectric etch process. The prior art entitled Aerosol Substrate Cleaner, Fishkin et. al., Pat. #6,332,470 talks about using vapor only or in conjunction with high pressure liquid droplet for cleaning semiconductor substrate. Unfortunately, the liquid impact does not have sufficient momentum transfer capability as the solid CO_2 and will therefore not be as effective in removing the small particles for which the ratio of force of adhesion to removal increases. Residue Removal by Supercritical Fluids, McCullough, et. al., Pat. #5,908,510 talks of an idea of using cryogenic aerosol in conjunction with supercritical fluid or liquid CO_2. Since CO_2 is a non-polar molecule the solvation capability of polar FM is significantly reduced. Also since the liquid or supercritical CO_2 formation requires high pressure (greater than 75 psi for liquid and 1080 psi for supercritical), the equipment becomes expensive.

SUMMARY OF THE INVENTION

The invention proposes the use of a reactive gas to chemically react with the FM along with the physical removal mechanism of the CO_2 snow cleaning.

The reactive vapor will be able to penetrate the submicron vias and trenches and chemically react with the FM to remove them.

The reactive vapor will also be able to chemically react with the FM on the surface to aid in their removal using the physical mechanism of CO_2 snow cleaning

DETAILED DESCRIPTION

In semiconductor wafer cleaning processes, the FM to be removed include films of organic, inorganic, and metal-organic residues at various steps both at FEOL and BEOL processes. These films cannot be removed by purely physical mechanism and a chemical assisted to any physical mechanism of removal is required to meet cleanliness needs. The two working in tandem or in sequence is able to completely remove the FM.

This invention incorporates a reactive vapor clean with or without the assistance of free radical initiator such as ultra violet light (UV), X-ray, Excimer laser, or corona discharge to generate reactive chemical species combined with physical cleaning of CO_2 snow or cryogenic aerosols to remove the non reactive FM. Similar cleaning mechanism is seen in wet cleaning and dual frequency plasma cleaning using downstream MW plasma to generate the chemical species for reaction with the contaminant and RF plasma to generate the ion bombardment.

One embodiment of this practice is done by spraying the surface with a vapor before or in conjunction with the snow cleaning. The nozzle can also have a corona discharge to generate free radicals in the vapor which will assist with chemical reaction with the residual film. Alternatively, X-rays, UV light, or Excimer lasers can be used to generate the radicals from the gas or vapor.

[1]. Particle Control for Semiconductor Manufacturing, Ed. R. P. Donovan, Marcel Dekker Inc., NY, 1990.
[2]. Handbook of Semiconductor Wafer Cleaning Technology, Ed. Werner Kern, Noyes Publications, NJ, 1993.

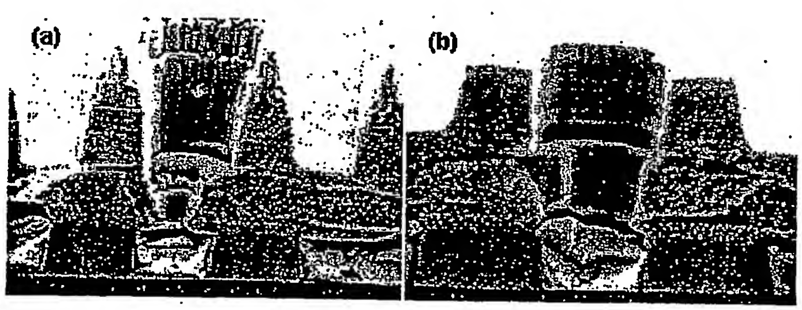

Figure 1. Cleaning of the post-trench etch residues in a dual-damascene structure. The left image is the SEM of the post-trench etch structure with etch residues present. The right image is the SEM of the post-trench etch structure after a sequence of plasma and wet clean steps. Source: Semiconductor International, July 1, 2001